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GLUTAMIC ACID REVIEW AND BIBLIOGRAPHY

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REVIEW

Production and use as a condiment of the monosodium salt of glutamic acid originated, according to Han, in Japan about 1908. Previously, protein hydrolysates were widely used throughout the Orient as flavoring materials for predominantly vegetarian diets. The desirable meat-like flavor of these hydrolysates was found to be due largely to the glutamic acid, the monosodium salt of which is so effective that the taste threshold is 1:3000, as compared with 1:200 for cane sugar and 1:400 for table salt. The development of what has been a laboratory curiosity into an article of commerce was therefore quite justified.

Little interest was shown in this development by American industry until the early 1930's, although it had been mentioned in the patent literature as early as 1912. The industrial capacity to produce monosodium glutamate was not sufficient to meet the increased requirements for canned and dehydrated foods in World War II; consequently, interest in the product and in its production have been widespread. It is obtainable both from Steffen's waste, a by-product of beet sugar manufacture, and from wheat gluten, by-product of starch and alcohol production from wheat. Wheat, frequently grown in excess of food requirements in prewar years, has presented a persistent problem of economical utilization.

Chemical structure

Glutamic acid is alpha-amino glutaric acid:

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              H    H    H
HO - C - C - C - C* - C - OH
     "   H    H    N     "
     O            H H    O
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The starred carbon atom is assymetric; hence glutamic acid occurs in two forms, one levo-rotatory, the other dextro-rotatory. However, because the dextro-rotatory form has been shown to belong configurationally to a group of compounds which contain the naturally occuring amino acids, most of which are levo-rotatory, it is correctly designated as l(+) glutamic acid, the "l" indicating the family compounds to which it belongs and the (+) the direction of rotation. The optical isomer is called d(-) glutamic acid. In many patents and papers the dextro compound is written simply d-glutamic acid; l(+)glutamic acid is meant.

A mixture of equal parts of l(+)-and d(-)glutamic acid is optically inactive and is called racemic or dl-glutamic acid.

Occurrence

Glutamic acid occurs in nature mostly as the l(+) isomer. A major constituent of most proteins, it occurs to some degree in practically all (See Table I). The monoamide, l-glutamine, is found in plant and animal tissues. Folic acid, a vitamin, contains glutamic acid. A major commercial source is beet extract from which the sucrose has been removed (Steffen's waste). A tri-peptide, glutathione, containing glutamic acid, is also a constituent of living tissue.

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The occurrence of d(-)glutamic acid is limited. The only proven natural source is a polypeptide of d(-)glutamic acid elaborated by a specific strain of B. subtilis. Other bacterial end-products are known to contain the unnatural forms of other amino acids and it may be expected that the d(-)glutamic acid will be isolated from some of these.

Kögl and his collaborators reported that cancer tissues contain appreciable amounts of unnatural amino acids, particularly d(-) glutamic acid. The results of considerable research investigation that was stimulated by the theory have not confirmed this claim.

Synthesis of glutamic acid

A number of investigators have succeeded in synthesizing glutamic acid from simpler organic substances. The more recent syntheses are based on malonic ester and acetoacetic ester methods. The products are optically inactive and hence contain only 50% of the desired l(+) isomer. At the present time it appears that l(+)glutamic acid can be obtained more economically from natural sources than by synthesis in the laboratory.

Resolution

The separation of optical isomers of amino acids is usually a lengthy and laborious task. It can be accomplished by careful fractionation of the salts of amino acids with optically active alkaloids. Sugasawa resolved dl-glutamic acid by converting it to dl-pyrrolidone carboxylic acid, preparing and then fractionating the quinine salts, and reconverting the isomers to glutamic acid. d(-) glutamic acid has been prepared from dl-glutamic acid by enzymatic resolution.

Racemization

Racemization is the term applied to the change of an optically active substance to its inactive form. This transformation is to be avoided in the manufacture of l(+)glutamic acid inasmuch as d(-)glutamic acid does not possess the unique flavor of its isomer, and the net result is a loss of flavor. Racemization occurs much more readily in alkaline than in acid solutions. Boiling 20% hydrochloric acid will racemize approximately 2-4% of l(+)glutamic acid in 24 hours. With the same time and temperature of heating, 30% is racemized by 20% sodium hydroxide.

Preparation from wheat gluten

In one method of preparing glutamic acid from wheat gluten, the protein is completely hydrolyzed by boiling or autoclaving with strong hydrocloric acid. The humin is then removed by filtration. Decolorization may be effected by heating with carbon. The excess hydrochloric acid is removed by evaporation at reduced pressure. Glutamic acid hydrochloride crystallizes from the concentrated, strongly acid hydrolysate.

The crystalline hydrochloride is dissolved in water, treated with charcoal to remove residual color, filtered, and carefully adjusted to pH 3.3, the isoelectric point of glutamic acid. Glutamic acid crystallizes.

In order to obtain the monosodium salt, the glutamic acid is brought to pH 7.0 in aqueous solution with sodium hydroxide. Upon concentration, the monosodium salt crystallizes. This salt is the article of commerce. Its taste and purity depend upon the care which has been taken in the previous steps. There is only

meager information about yields. Commercial recoveries possibly amount to approximately 20% by weight of the gluten used, or from $\frac{1}{2}$ to 2/3 of the glutamic acid known to be present.

Preparation from other proteins

Corn gluten and soy bean protein have been advocated as sources of glutamic acid. With these proteins, the percentage of recovery appears to be even lower than with wheat gluten.

Preparation from Steffen's waste

Steffen's waste is the spent liquor remaining after the extraction of sugar from sugar beet molasses by Steffen's process. Some Steffen's waste contains amounts of glutamic acid which make practical its isolation from this source. Other lots may contain little or no glutamic acid. The reasons for the differences are obscure although it is known that beets from certain geographical localities are consistently high, and from others low, in glutamic acid.

Careful alkaline hydrolysis is used with Steffen's waste to obtain the glutamic acid from its precursor, possibly pyrrolidone carboxylic acid. Several patented procedures are described for the isolation steps.

Condiment

The taste of most samples of monosodium glutamate is meat-like. When a few crystals are placed in the mouth, there is no immediate sensation. Then the taste of good beefsteak develops slowly, mostly in the rear of the mouth, and persists for some time. It is claimed that monosodium glutamate, like salt, enhances other flavors, in addition to possessing one of its own. A very highly purified sample of monosodium glutamate has a more delicate flavor than those usually marketed, suggesting that the more gross, meat-like flavor may be an impurity.

Nutrition

Glutamic acid is usually classed as one of the non-essential amino acids. However, it has been maintained that its inclusion in the diet of chickens is necessary for best growth.

Approximate glutamic acid content
of natural materials.

Protein	Glutamic Acid Content*
	per cent
Gliadin	46
Gluten	36
Zein	26
Casein	22
Insulin	20
Beta-lactoglobulin	19
Edestin	19
Bovin serum albumin	17
Egg albumin	16
Fibrin	13
Gelatin	12

Protein	Glutamic Acid Content* per cent
Steffen's waste	0-15**
Silk fibroin	2

* Dry basis

**The glutamic acid content of Steffen's waste may vary widely depending upon geographical location of the beet-growing area and other as yet unidentified factors.

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